

10/593029

IAP12 Rec'd PCT/PTO 15 SEP 2006

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No. :

U.S. National Serial No. :

Filed :

PCT International Application No. : PCT/EP2005/002741

VERIFICATION OF A TRANSLATION

I, Neil Thomas SIMPKIN BA,

Acting Deputy Managing Director of RWS Group Ltd, of Europa House, Marsham Way,  
Gerrards Cross, Buckinghamshire, England declare:

That the translator responsible for the attached translation is knowledgeable in the German language in which the below identified international application was filed, and that, to the best of RWS Group Ltd knowledge and belief, the English translation of the international application No. PCT/EP2005/002741 is a true and complete translation of the above identified international application as filed.

I hereby declare that all the statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application issued thereon.

Date: August 17, 2006

Signature :



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Oxygen-bridged bimetallic complex, the production thereof and its utilization for polymerization catalysis

- 5 The invention relates generally to the field of transition metal complex catalysts and metallocene catalysts for olefin polymerization.

10 Transition metal catalysts of the Ziegler-Natta type or catalyst systems developed therefrom have for a long time been widely used industrially as catalysts for low-pressure olefin polymerization, in particular the stereoselective polymerization of  $\alpha$ -olefins. Chiral metallocene catalysts play an important role.

15

Cocatalysts used are organoaluminum compounds such as trialkylaluminum, alkylhaloaluminum, e.g.  $\text{AlEtCl}_2$  or  $\text{AlEt}_2\text{Cl}$ , or, very widely, alkylaluminoxanes, in particular methylaluminoxane (MAO). To be able to achieve  
20 optimal catalytic activity for the respective system, a large excess of MAO cocatalyst is required. Thus, it is known that the catalytic activity of zirconocene-MAO systems decreases drastically below an Al:Zr ratio of about 200-300:1. It would therefore be desirable to  
25 have a catalyst which can be combined with smaller amounts of cocatalyst.

Since the mechanism of olefin polymerization catalyzed by transition metals is, like the structure of MAO,  
30 very complex and therefore not completely elucidated (Angew. Chem. 1995, 107, 1255-1283: "Stereospezifische Olefinpolymerisation mit chiralen Metallocencatalysatoren", H-H. Brintinger, D. Fischer, R. Mülhaupt, B. Rieger and R. Waymouth), the targeted design of such  
35 complexes is difficult. A wide variety of catalyst systems have been tried with varying success. The production of stereochemically very uniform polymers having a narrow molecular weight distribution and also

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a good operating life of the catalysts used are frequently desired.

It is an object of the invention to discover complexes having good catalytic activity in the polymerization of, in particular, olefins, which complexes avoid the disadvantages known in the prior art and have good operating lives and can be used particularly economically.

10

The invention achieves this object by providing suitable novel binuclear, oxygen-bridged, bimetallic complexes of the general formula (I):

15 (I)  $[(LM^1R^1)(Cp_2M^2R^2)](\mu-O)$

where:

$M^1 = Al, Ge, Zr$  or  $Ti$ ;

$M^2 = Zr, Ti$  or  $Hf$ ;

20  $Cp =$  cyclopentadienyl;

$R^1, R^2 = H$ ;  $C(1-6)$ alkyl; halogen; aryl;  $SiMe_3$  and alkyl-aryl where aryl =  $C_6H_5-nX_n$  and  $X =$  halogen,  $C(1-6)$ alkyl, aryl,  $NO_2$ ,  $SO_3H$ ,  $NR^3_2$ , where  $R^3 = C(1-6)$ alkyl or  $H$  and  $n = 0$  to  $5$ ; and  $L$  is a bidentate, doubly heteroatom-coordinated organochemical ligand which together with the metal  $M^1$  forms a 5- or 6-membered ring. The heteroatom is preferably a nitrogen atom.

25

$M^1$  is preferably a main group metal, more preferably  $Al$  or  $Ge$ .

30

Possible halogens or halides are first and foremost chlorine, fluorine and bromine. As alkylphenyls, it is possible to use, in particular, monotrialkylphenyls, dialkylphenyls or trialkylphenyls.  $C(1-6)$ alkyl is any branched or unbranched alkyl radical having from 1 to 6 carbon atoms, preferably methyl, ethyl, i-propyl, n-propyl or t-butyl. Aryl is a benzene radical bearing

35

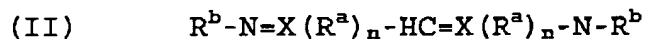
from 1 to 6 substituents and encompasses phenyl. The aryl substituents can preferably be selected from the group consisting of halogen, C(1-6)alkyl, aryl, NO<sub>2</sub>, SO<sub>3</sub>H, NR<sup>3</sup><sub>2</sub>, where R<sup>3</sup> = C(1-6)alkyl or H. In addition to  
 5 phenyl, another preferred radical is mesityl.

It has surprisingly been found that the novel complexes are excellent polymerization catalysts, as will be demonstrated below with the aid of practical experi-  
 10 mental data.

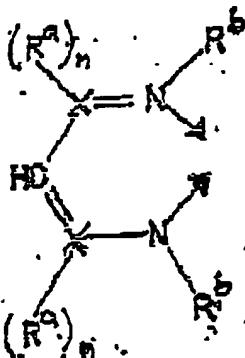
Preferred examples of the complexes of the invention are heterobimetallic complexes, in particular oxygen-bridged aluminum-zirconocene complexes, preferably com-  
 15 plexes of the general formula [(LAlMe)(Cp<sub>2</sub>ZrR<sup>2</sup>)](μ-O), where R<sup>2</sup> is Me or Cl.

The ligand L preferably has the following composition of the formula II

20



corresponding to the structural formula:



25

where: X = C or P;

R<sup>a</sup> and R<sup>b</sup> can be the same radicals as indicated for R<sup>1</sup> and R<sup>2</sup>, preferably H, methyl, ethyl, i-propyl, t-butyl,

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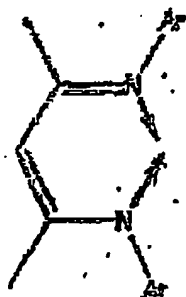
phenyl, alkylphenyl; trimethylsilyl;

$n = 1$  when  $X = C$ ;  $n = 2$  when  $X = P$ .

The ligand more preferably has the composition

5  $Ar-\underline{N}=C(CH_3)-HC=C(CH_3)-\underline{N}-Ar$ , where  $Ar = 2,6-iPr_2C_6H_3$

corresponding to the structural formula:



10

where  $Ar$  is an aromatic system and is in particular 2,6- $iPr_2C_6H_3$ .

15 To prepare the oxygen-bridged bimetallic complexes of the invention, we have found a process which is characterized in that a precursor complex of the formula  $LM^1R^1(OH)$  is reacted with a metallocene precursor complex  $Cp_2M^2(R^2)_2$  or  $Cp_2M^2MeR^2$  or  $Cp_2M^2HX$ , where  $X =$  halogen, preferably in an inert solvent.

20 Possible halogens are first and foremost fluorine, chlorine or bromine. Examples of the processes of the invention for preparing the complexes are given in the experimental part. These processes are also suitable for preparing heterobimetallic complexes in a targeted  
25 manner.

The invention also encompasses the use of binuclear, oxygen-bridged bimetallic, in particular heterobimetallic, complexes which have been formed from a  
30 transition metallocene and an organic Al, Ge, Zr or Ti

compound which does not contain a cyclopentadienyl group, in particular a complex as claimed in any of claims 1 to 4, as polymerization catalysts. The complexes are particularly suitable for the homopolymerization or copolymerization of olefins, including  $\alpha$ -olefins and cyclic olefins, for the cyclopolymerization of dienes and, if appropriate, for the polymerization of functionalized olefins. These catalysts are preferably used for the polymerization of low-pressure polyethylene.

As cocatalyst, preference is given to using a cocatalyst of the  $[\text{MeAlO}]_x$  type, in particular methylaluminoxane (MAO), or else trialkylaluminum or an alkylhaloaluminum compound.

The invention therefore also encompasses catalyst preparations for the polymerization of olefins, which preparations comprise at least a binuclear, oxygen-bridged, bimetallic complex according to the invention and at least one cocatalyst. Preference is given to using alkylaluminoxanes and in particular methylaluminoxane (MAO) as cocatalysts. Among the catalyst complexes according to the invention, preference is given to the heterobimetallic complexes.

As demonstrated by the experimental results, the catalyst complexes of the invention display very good catalytic activity. They reach a stable activity plateau within a short time and have good operating lives. It is surprising that the amount of cocatalyst (in the example MAO) required can be reduced by a multiple with the aid of the complexes of the invention, in the example polymerizations carried out by up to 90%, compared to the  $\text{Cp}_2\text{ZrMe}_2$  employed as reference.

#### Experimental part - Examples

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The preparation of example compounds is described below. The catalytic activity of these in the polymerization of ethylene was then examined. Here, the amount of cocatalyst was varied within a wide range.

A description of how  $\text{LAlMe(OH)}$  (2) can be obtained from the precursor compound  $\text{LAlMeCl}$  (1) by two different reaction routes will be given first.

10

The precursor compound (1) itself was synthesized as follows from commercially available starting materials:

**Synthesis of  $\text{LAlMeCl}$  (1):**  $\text{LLi} \cdot \text{OEt}_2$  (2.49 g, 5.00 mmol) in toluene (30 ml) was added dropwise to  $\text{MeAlCl}_2$  (5.00 ml, 1.0 M in hexane, 5.00 mmol) in toluene (15 ml) at  $-60^\circ\text{C}$ . The mixture was warmed to room temperature and stirred for 12 hours. Volatile constituents were removed under reduced pressure and the crude product was dissolved in hexane (100 ml). The finished solution was concentrated to 50 ml and allowed to stand overnight at  $-32^\circ\text{C}$  in order to obtain colorless crystals. An additional amount of 1 could be recovered from the mother liquor. Yield: (2.05 g, 83%).

Mp:  $190^\circ\text{C}$ ,  $^1\text{H NMR}$  (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 7.15-7.05 (m, Ar), 4.98 (s, 1 H,  $\gamma\text{-CH}$ ), 3.76 (sept,  $^3J_{\text{HH}} = 6.8$  Hz, 2 H,  $\text{CHMe}_2$ ), 3.21 (sept,  $^3J_{\text{HH}} = 6.8$  Hz, 2 H,  $\text{CHMe}_2$ ), 1.52 (s, 6H, CMe), 1.46 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 6 H,  $\text{CHMe}_2$ ), 1.28 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 6 H,  $\text{CHMe}_2$ ), 1.19 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 6 H,  $\text{CHMe}_2$ ), 1.02 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 6 H,  $\text{CHMe}_2$ ), -0.65 (s, 3 H, AlMe); EI-MS: m/e (%); 479 (100) [ $\text{M}^+ - \text{Me}$ ]; elemental analysis, calculated for  $\text{C}_{30}\text{H}_{44}\text{AlClN}_2$  (494): C 72.9, H 8.9, N 5.6; found: C 72.8, H 9.0, N 5.6.

The  $\text{LAlMe(OH)}$  (2) is reacted with zirconocenes (bis( $\eta$ -cyclopentadienyl)zirconium complexes) to form two different complexes, namely  $[(\text{LAlMe})(\text{Cp}_2\text{ZrMe})](\mu\text{-O})$  (3) and  $[(\text{LAlMe})(\text{Cp}_2\text{ZrCl})](\mu\text{-O})$  (4).

The associated reaction equations are shown in the figures.

5 In the figures:

Fig. 1 shows the preparation of  $\text{LAlMeCl}$  from  $\text{LLiOEt}_2$  and  $\text{MeAlCl}_2$ ;

10 Fig. 2a shows the preparation of  $\text{LAlMe(OH)}$  from  $\text{LAlMeCl}$  using  $\text{KH}$  in a strongly basic medium;

Fig. 2b shows the preparation of  $\text{LAlMe(OH)}$  from  $\text{LAlMeCl}$  using 1,3-di-*t*-butylimidazole,

15 Fig. 3 shows the preparation of  $[(\text{LAlMe})(\text{Cp}_2\text{ZrMe})](\mu\text{-O})$  from  $\text{LAlMe(OH)}$  and  $\text{Cp}_2\text{ZrMe}_2$ .

Fig. 4 shows the preparation of  $[(\text{LAlMe})(\text{Cp}_2\text{ZrCl})](\mu\text{-O})$  from  $\text{LAlMe(OH)}$  and  $\text{Cp}_2\text{ZrHCl}$ .

20 Fig. 5 shows a plot of TOF values for catalyst 3 compared to the reference catalyst;

Fig. 6 shows a plot of reaction rates;

Fig. 7 shows the influence of the cocatalyst/catalyst ratio on the reaction rate.

## 25 General

All handling was carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. The samples for the recording of spectra and for  
30 reactions were processed in a glove box. The solvent was dried, distilled under nitrogen and degassed by customary methods before use.

The  $^1\text{H}$ -NMR spectra were recorded on a Bruker AM 200  
35 nuclear magnetic resonance spectrometer using  $\text{SiMe}_4$  as external standard. The mass spectra were recorded on a Finnigan MAT 8230 mass spectrometer using the EI-MS method. The strongest peak of an isotope distribution



is tabulated. The IR spectra were recorded in Nujol between KBr plates on a Bio-Rad FTS-7 spectrometer. The elemental analyses were carried out at the analytical laboratory of the Institute for Inorganic Chemistry of the University of Göttingen.

Synthesis of the precursor complex LAlMe(OH) (2): 40 ml of ammonia were condensed onto a suspension of LAlMeCl (1, 1.98 g, 4.00 mmol), KOH (KOH > 85%, H<sub>2</sub>O 10-15%, 0.15 g, 2.33 mmol of KOH (85%), 1.28 mmol of H<sub>2</sub>O (15%)) and KH (0.05 g, 1.25 mmol) in toluene (80 ml) at -78°C while stirring. The mixture was stirred at this temperature for a further one hour. The excess ammonia was then allowed to evaporate from the reaction mixture over a period of 4 hours. During this time, the mixture was slowly warmed to room temperature. After filtration and subsequent concentration under reduced pressure (to 8 ml), the resulting colorless solution was kept at -20°C for one week in order to isolate the colorless crystals of 2 (1.12 g). After separating off the crystals and subsequent partial removal of the solvent from the mother liquor, the colorless solution obtained was kept at -20°C for two days, and an additional yield of 2 (0.19 g) was recovered. Total yield: 1.31 g (68%, measured on 1). M.p.: 192°C; IR (Nujol)  $\tilde{\nu}$  = 3728, 1552, 1530, 1373, 1316, 1256, 1189, 1178, 1106, 1056, 1023, 940, 878, 805, 768, 757, 689, 614 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 7.16-7.07 (m, Ar), 4.93 (s, 1 H,  $\gamma$ -CH), 3.69 (sept, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 2 H, CHMe<sub>2</sub>), 3.25 (sept, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 2 H, CHMe<sub>2</sub>), 1.57 (s, 6 H, CMe), 1.32 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 12 H, CHMe<sub>2</sub>), 1.21 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6 H, CHMe<sub>2</sub>), 1.07 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6 H, CHMe<sub>2</sub>), 0.53 (s, 1 H, OH); -0.88 (s, 3 H, AlMe); EI-MS: m/e (%); 461 (100) [M<sup>+</sup> - Me]; elemental analysis: calculated for C<sub>30</sub>H<sub>45</sub>AlN<sub>2</sub>O (476.7): C 75.6, H 9.5, N 5.9; found: C 75.4, H 9.5, N 6.0.

Alternative synthesis of 2 from 1: 1,3-Di-tert-butyl-

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imidazol-2-ylidene (1.08 g, 6.00 mmol) in toluene (50 ml) were added to  $\text{LiAlMeCl}$  (2.97 g, 6.00 mmol) in toluene (80 ml). The solution was stirred at room temperature for 10 minutes. Degassed and distilled water (108  $\mu\text{l}$ , 6.00 mmol) was slowly added over a period of 30 minutes while stirring. The mixture was stirred for a further one hour. Volatile components were removed under reduced pressure and the crude product was extracted in hexane (150 ml), with the 1,3-di-tert-butylimidazolium chloride being filtered off through Celite. The solution finally obtained was concentrated (60 ml) and stored at  $-20^\circ\text{C}$  for two days in order to give colorless crystals. Yield: 2.45 g (86%).

15

Synthesis of  $[(\text{LiAlMe})(\text{Cp}_2\text{ZrMe})](\mu\text{-O})$  (3): Toluene (60 ml) was added to a mixture of 2 (0.48 g, 1.00 mmol) and  $\text{Cp}_2\text{ZrMe}_2$  (0.25 g, 1.00 mmol). The mixture was stirred at room temperature for 2 hours and then at  $100^\circ\text{C}$  for 24 hours. The resulting colorless solution was kept at room temperature for 48 hours in order to isolate colorless crystals of 3 (0.51 g). After concentrating the filtrate to 8 ml, the solution was kept at  $0^\circ\text{C}$  for three days. A further 0.15 g of 3 was obtained. Yield: 0.66 g (93%). M.p.:  $385^\circ\text{C}$  (dec); IR (Nujol)  $\tilde{\nu}$  = 1518, 1467, 1380, 1316, 1257, 1178, 1101, 1017, 936, 884, 798, 768, 643, 617, 449  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.25-7.24 (m, Ar), 5.31 (s, 10 H, Cp), 5.06 (s, 1 H,  $\gamma\text{-CH}$ ), 3.17 (sept,  $^3J_{\text{HH}}$  = 6.8 Hz, 2 H,  $\text{CHMe}_2$ ), 3.15 (sept,  $^3J_{\text{HH}}$  = 6.8 Hz, 2 H,  $\text{CHMe}_2$ ), 1.75 (s, 6 H, CMe), 1.37 (d,  $^3J_{\text{HH}}$  = 6.8 Hz, 6 H,  $\text{CHMe}_2$ ), 1.35 (d,  $^3J_{\text{HH}}$  = 6.8 Hz, 6 H,  $\text{CHMe}_2$ ), 1.22 (d,  $^3J_{\text{HH}}$  = 6.8 Hz, 6 H,  $\text{CHMe}_2$ ), 1.03 (d,  $J_{\text{HH}}$  = 6.8 Hz, 6 H,  $\text{CHMe}_2$ ), -0.32 (s, 3 H, ZrMe), -0.72 (s, 3 H, AlMe); EI-MS: m/e (%): 695 (100) [ $\text{M}^+ - \text{Me}$ ]; elemental analysis: calculated for  $\text{C}_{41}\text{H}_{57}\text{AlN}_2\text{OZr}$  (712.1): C 69.2, H 8.1, N 3.9; found: C 69.3, H 7.9, N 3.9.

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Synthesis of [(LAlMe)(Cp<sub>2</sub>ZrCl)](μ-O) (4): In a procedure similar to that used for the preparation of 3, toluene (60 ml) was added to a mixture of 2 (0.48 g, 1.00 mmol) and Cp<sub>2</sub>ZrHCl (0.25 g, 1.00 mmol). The colorless solution obtained was kept at room temperature for 48 hours in order to isolate colorless crystals of 4 (0.37 g). After concentrating the filtrate to 10 ml, the solution was kept at 0°C for three days. A further 0.28 g of 4 was obtained. Yield: 0.65 g (89%). M.p.: 396°C (dec); IR (Nujol)  $\tilde{\nu}$  = 1530, 1466, 1380, 1315, 1254, 1181, 1098, 1022, 943, 860, 797, 778, 759, 725, 657, 617 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.29-7.21 (m, Ar), 5.54 (s, 10 H, Cp), 5.09 (s, 1 H, γ-CH), 3.16 (sept, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 2 H, CHMe<sub>2</sub>), 3.15 (sept, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 2H, CHMe<sub>2</sub>), 1.78 (s, 6 H, CMe), 1.42 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6 H, CHMe<sub>2</sub>), 1.36 (d, <sup>3</sup>J<sub>HH</sub> = 6.8, 6 H, CHMe<sub>2</sub>), 1.24 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6 H, CHMe<sub>2</sub>), 1.02 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6 H, CHMe<sub>2</sub>), -0.66 (s, 3 H, AlMe); EI-MS: m/e (%): 715 (100) [M<sup>+</sup> - Me]; elemental analysis: calculated for C<sub>40</sub>H<sub>54</sub>AlClN<sub>2</sub>OZr (732.5): C 65.6, H 7.4, N 3.8; found: C 65.5, H 7.3, N 3.9.

#### Polymerization of ethylene

Catalyst (0.005 M in toluene, 4 ml, 20 μmol) was added to toluene (100 ml) in a 250 ml Schlenk flask. This solution was degassed and the system was then connected to an ethylene atmosphere (1013 mbar pressure). The associated aluminoxane (toluene solution) was added. After the mixture obtained had been stirred for an appropriate time, the reaction was stopped by means of ethanol and the white polyethylene (PE) was collected and dried. The results are shown in Table 1 and Figure 5.

35

#### Determination of the TOF and the polymerization rate

g gram of polyethylene were obtained in 0.5 hours. The

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TOF was then calculated according to:

$$\text{TOF} = \frac{\text{g of PE}}{20 \times 10^{-6} (\text{mmol of cat}) \times 0.5 (\text{h})} = \frac{\text{g}}{10} \times 10^6 (\text{g of PE/mol cat h})$$

- 5 When the ethylene volume V (consumed when the pressure of the system has dropped to 27 mbar below atmospheric pressure) has been polymerized in t seconds (when t is less than 1 sec, it is difficult to determine the reaction time precisely), the reaction rate is  $r = V/t$   
10 (Table 2 and Figure 6).

#### Influence of the concentration of 3 on the TOF

- 15 Explanations of the data in Table 1: using the method as described above, 3 (0.005 M in toluene, 3 ml, 15  $\mu\text{mol}$ ), for example, was added to toluene (100 ml). MAO (0.15 ml) was added while stirring. After 20 minutes, MAO (1.5 ml) was added and the polymerization was started. After the resulting mixture had been  
20 stirred for 30 minutes, PE (9.9 g) was obtained (Experiment No. A08). Using the same method, MAO (0.1 ml) was added to a solution of 3 (2 ml, 10  $\mu\text{mol}$ ). After 20 minutes, MAO (1.0 ml) was added again. After polymerization for 2 hours, PE (7.6 g) was obtained  
25 (Experiment No. A09). The results and conditions for various experiments are summarized in Table 1. The experiments denoted by A and B relate to the catalysts according to the invention, and the experiments denoted by D relate to reference experiments.

30

#### Influence of the reaction time of 3 with MAO on the TOF

- Using the same method, 1.7 ml or 3.4 ml of MAO were added to 3 (20  $\mu\text{mol}$ ). After 18 or 30 minutes, 6.2 g or  
35 10.9 g, respectively, of PE were obtained (Experiment No. A 10 and A 11 in Table 1).

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The tabular data for 3 and the reference example are shown graphically in Figure 5. It can be seen that the novel catalyst achieves a high value of the TOF even at very much smaller amounts of cocatalyst.

5

In Figure 6, the reaction rate is plotted against the reaction time for 5 catalyst mixtures (A) with MAO and, for comparison, three  $\text{Cp}_2\text{ZrMe}_2$  (D) systems with MAO. It can be seen that the novel catalyst mixtures (A07-A03) show constant behavior as a function of time, while this is not the case for the known ( $\text{Cp}_2\text{ZrMe}_2$ ) mixtures.

In Figure 7, the reaction rate is plotted as a function of the reaction time. Once for the novel catalyst system and MAO (A02) in a ratio of MAO to catalyst of 48:1 and, for comparison,  $\text{Cp}_2\text{ZrMe}_2$  in a ratio of MAO to catalyst of 176:1 (D05). It can clearly be seen that the novel system A02 still has about twice the reaction rate after 60 minutes. It has to be noted that only about a quarter of the amount of MAO was used in the novel A02 system.

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Table 1: TOF (g of PE/mol of cat·h × 10<sup>-6</sup>) values for catalysts 3, 4 and Cp<sub>2</sub>ZrMe<sub>2</sub>

Catalyst*	MAO:cat	t (min)	PE (g)	TOF
3 (A01)	32	60	0.89	0.05
3 (A02)	48	60	7.8	0.39
3 (A03)	96	30	9.0	0.90
3 (A04)	136	30	10.9	1.09
3 (A05)	176	30	11.9	1.19
3 (A06)	272	30	12.4	1.24
3 (A07)	400	30	12.7	1.27
3 (A08)	176	30	9.9	1.32
3 (A09)	176	120	7.6	0.39
3 (A10)	136	18	6.2	1.03
3 (A11)	272	30	10.9	1.09
4 (B04)	136	30	8.4	0.84
4 (B05)	176	30	11.4	1.14
Cp <sub>2</sub> ZrMe <sub>2</sub> (D04)	136	120	3.3	0.08
Cp <sub>2</sub> ZrMe <sub>2</sub> (D05)	176	73	12.8	0.52
Cp <sub>2</sub> ZrMe <sub>2</sub> (D06)	272	60	14.6	0.73
Cp <sub>2</sub> ZrMe <sub>2</sub> (D07)	400	37	14.8	1.20

5

\*For Experiments A01 to A07, 0.2 ml of MAO was added to a solution containing 3. After 20 minutes, the remaining MAO was added and the polymerization was started.

Table 2. Polymerization reaction rates  $r$  (V/sec.) for the catalysts 3 and  $\text{Cp}_2\text{ZrMe}_2$ 

A03		A04		A05		A06		A07		D05		D06		D07	
t	r	t	r	t	r	t	r	t	r	t	r	t	r	t	r
0.96	0.03	1.33	0.04	0.85	0.08	0.68	0.07	0.20	0.08	2.10	0.043	0.98	0.13	1.97	0.20
2.52	0.05	2.92	0.07	1.98	0.13	1.62	0.13	1.10	0.20	4.00	0.045	3.23	0.14	4.50	0.25
4.21	0.08	4.23	0.11	2.42	0.16	2.60	0.25	1.40	0.25	6.85	0.053	5.25	0.17	6.80	0.33
5.72	0.13	5.96	0.20	3.30	0.25	3.18	0.33	1.75	0.33	10.50	0.067	6.83	0.20	8.70	0.50
6.96	0.20	6.69	0.25	3.90	0.33	3.52	0.42	2.03	0.40	15.85	0.091	8.23	0.25	10.92	1.00
7.67	0.25	7.68	0.33	4.30	0.40	4.30	0.67	2.27	0.50	21.48	0.125	10.63	0.33	12.18	1.00
8.98	0.33	8.95	0.50	5.75	0.80	4.83	0.92	2.72	0.67	24.90	0.143	13.00	0.50	14.80	0.50
11.37	0.50	9.80	0.77	6.60	1.00	5.35	1.00	3.58	1.00	28.00	0.167	17.93	1.00	19.33	0.40
13.92	0.67	10.38	1.00	10.70	1.00	9.56	1.00	8.25	1.00	30.88	0.200	22.88	0.50	30.00	0.33
15.58	0.72	12.97	1.00	12.80	0.67	11.25	0.78	11.50	0.07			25.78	0.33		
17.48	0.67	16.37	0.67	16.58	0.50	12.58	0.67	16.30	0.50			30.00	0.29		
21.00	0.50	20.77	0.40	19.30	0.44	15.30	0.54	17.91	0.46						
24.20	0.40	24.12	0.37	22.01	0.40	23.81	0.38	21.20	0.40						
29.48	0.33	30.00	0.33	29.59	0.37	29.95	0.35	30.00	0.35						